WSRC-MS-2001-00568

Balance Repeatability and Reproducibility Effects on Measurement Uncertainty

by

A. H. Shull

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

J. P. Clark

A document prepared for MEASUREMENT SCIENCE CONFERENCE at Anaheim, CA, USA from 1/24/2002 - 1/25/2002.

DOE Contract No. **DE-AC09-96SR18500**

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy

DISCLAIMER

Balance Repeatability and Reproducibility Effects on Measurement Uncertainty*

By:

A. Harper Shull & John P. Clark
Westinghouse Savannah River Company
Aiken, SC 29808

Abstract

Most balance manufacturers do not list an uncertainty estimate for measurements made with their balances. Their specifications usually include eccentricity, linearity, and repeatability. The latter is a measure of the random variability of the instrument, usually expressed in scale divisions. Further, the repeatability is usually based on 10 consecutive measurements of a mass standard. The authors have previously described methods currently being used to estimate the uncertainty of measurements made with electronic balances. [i] The random errors associated with mass measurements obscure the true value of the artifact being weighed. Therefore, it is important to include the best estimate of the magnitude of these errors in the stated uncertainty.

The random and systematic errors associated with weighing the same known mass standard were determined in a detailed experiment. An attempt was made to stabilize as many of the variables affecting the weighing procedure as possible. Each day, the balances were calibrated using their internal calibration procedure. Interfacing them with a computer allowed the first stable reading detected after placing the weight on the pan to be printed into a spreadsheet. Environmental conditions were recorded each day.

Day to day variation (reproducibility) in the averages of the balance repeatability measurements was often an order of magnitude greater than the repeatability specification listed by the manufacture. Therefore, it was important to determine the magnitude of this source of variation and include it the calculation of the uncertainty estimate. The purpose of an uncertainty estimate is to provide a range of values, having a specified confidence level that includes the true value of the weight measurement.

Introduction

The manufacturers of most analytical balances do not list a single numerical value as an estimate of the total uncertainty. Instead, estimates of sensitivity, eccentricity, linearity, and sometimes repeatability are given. There may be confusion as to the meaning of a stated repeatability value as to whether it is one, two or three standard deviations. In addition, repeatability is defined in VIM Vocabulary of Metrology 527(5.31) as the ability of a measuring instrument to provide closely similar indications for repeated applications of the same measurand under the same conditions of measurement. These conditions include: 1.Reduction to a minimum of the variations due to the observer; 2. The same measurement procedure; 3. The same observer; 4. The same measuring equipment, used under the same conditions; 5. The same location; 6. Repetition over a short period

- **The information contained in this article was developed during work under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy. To be published as WSRC-MS-2001-00568.**

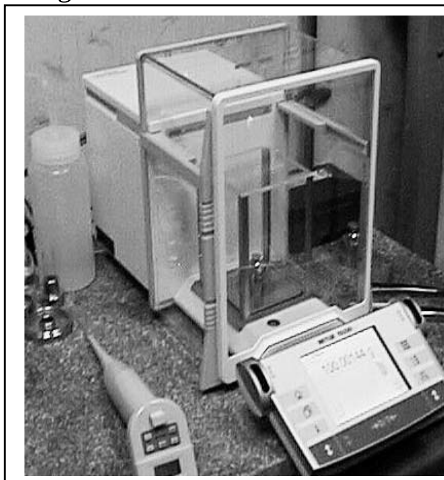
of time. Repeatability may be expressed quantitatively in terms of the dispersion characteristics of the indications as a short-term random standard deviation.

Another well accepted term used to describe variation is reproducibility. It is quite different from repeatability, as it is the variation that is observed when very few or none of the conditions described above are held constant during data collection. As a result, reproducibility includes both long and short-term random components and is therefore more representative of the variation actually experienced in day to day usage of the measuring instrument. It is obvious then that uncertainty of most instrumentation, including analytical balances, is a function of the environment in which they are used and how well it is or is not controlled. With these considerations, it was decided to undertake a long-term data collection experiment to provide an empirical estimate of the uncertainty of a balance in the standards laboratory at the Westinghouse Savannah River Technical Center.

Phase I - Experiment and Data Analysis

It was decided to perform the experiment on a new Mettler[R] AX205 5-place balance (See Figure 1), which had been recently purchased for pipette calibration work. Since the new purchased balance was scheduled for use in pipette calibration work, it was desired to adequately estimate the variability of the balance, as its uncertainty would impact the calibration uncertainty budget. The experiment would consist of repeated weighings of a 100-gram standard, which was half of the capacity of the balance. The actual calibrated weight of the standard was 100.00151 +/- 0.00012 with 95% confidence (2 standard deviations). The weighings would be taken once or more each working day as time allowed and would be spread over as many days as reasonable to provide good estimates of reproducibility. Replication "within" days as well as replication "between" days was desired to determine separate estimates of short-term (repeatability) and long-term random variation (reproducibility). [ii] It was decided that at least 20 sets of 10 replicates would be performed to provide adequate data for statistical analysis. Each set would consist of 10 replicates with a "zeroing" of the balance between each replication and an internal balance calibration performed before each set. The experiment began in February 2001 in an office/lab environment with the usual office-type heating and cooling, but no humidity control. Because the operating environment was not completely controlled, data on barometric pressure, temperature, and relative humidity were also collected at weighing times to determine their effect, if any, on the weighing variation.

Figure1 – Mettler[R] AX205 Balance



It soon became apparent that the balance was not operating normally as excessive variation was experienced. The mean of the 10 measurements varied significantly from day to day. Also, the observed variation was significantly greater than the manufacturer's +/- 0.00003-gram tolerance for repeatability. However, the experiment was continued until 22 days of measurements were taken to provide adequate data for statistical evaluation. This data and some summary statistics are shown in Table 1 below. As one can see, the variation in the daily average of 10 measurements varied as much as 0.34 milligrams, which is excessive for a 5-place AX205 balance. After contacting the distributor, the balance was returned to the manufacturer and replaced with the same type of balance by the distributor.

A thorough statistical analysis was completed on the weight data to provide estimates of short and long-term random balance variation as originally planned. Analysis of the environmental data will be discussed later.

Table 1 – Phase I Replicate Weight Data

Date	1	2	3	4	5	6	7	8	9	10	Average	Std. Dev.
2/15/01	100.00145	100.00144	100.00148	100.00148	100.00150	100.00148	100.00148	100.00161	100.00177	100.00177	100.00155	0.00012669
2/15/01	100.00155	100.00157	100.00168	100.00152	100.00152	100.00154	100.00154	100.00156	100.00158	100.00156	100.00156	0.00004590
2/15/01	100.00159	100.00158	100.00158	100.00155	100.00156	100.00155	100.00156	100.00153	100.00156	100.00157	100.00156	0.00001757
2/22/01	100.00174	100.00169	100.00169	100.00148	100.00146	100.00144	100.00150	100.00150	100.00150	100.00154	100.00155	0.00010948
2/22/01	100.00151	100.00150	100.00148	100.00150	100.00145	100.00155	100.00147	100.00153	100.00146	100.00152	100.00150	0.00003199
2/26/01	100.00140	100.00139	100.00137	100.00136	100.00136	100.00137	100.00134	100.00134	100.00133	100.00133	100.00136	0.00002426
2/26/01	100.00161	100.00162	100.00162	100.00167	100.00162	100.00165	100.00162	100.00165	100.00163	100.00158	100.00163	0.00002495
2/27/01	100.00150	100.00149	100.00149	100.00147	100.00151	100.00144	100.00151	100.00148	100.00143	100.00145	100.00148	0.00002863
2/28/01	100.00164	100.00166	100.00164	100.00164	100.00160	100.00158	100.00160	100.00157	100.00159	100.00157	100.00161	0.00003316
3/01/01	100.00171	100.00169	100.00164	100.00171	100.00167	100.00164	100.00165	100.00156	100.00169	100.00164	100.00166	0.00004496
3/05/01	100.00157	100.00157	100.00154	100.00154	100.00144	100.00150	100.00140	100.00146	100.00143	100.00145	100.00149	0.00006202
3/06/01	100.00144	100.00140	100.00152	100.00145	100.00145	100.00147	100.00148	100.00143	100.00146	100.00143	100.00145	0.00003267
3/07/01	100.00152	100.00155	100.00155	100.00156	100.00160	100.00159	100.00157	100.00160	100.00160	100.00159	100.00157	0.00002751
3/07/01	100.00154	100.00155	100.00147	100.00149	100.00156	100.00148	100.00151	100.00149	100.00148	100.00152	100.00151	0.00003217
3/08/01	100.00156	100.00146	100.00148	100.00148	100.00143	100.00145	100.00146	100.00148	100.00145	100.00146	100.00147	0.00003510
3/12/01	100.00152	100.00159	100.00155	100.00153	100.00159	100.00155	100.00154	100.00156	100.00156	100.00157	100.00156	0.00002313
3/13/01	100.00143	100.00147	100.00149	100.00144	100.00143	100.00150	100.00139	100.00144	100.00148	100.00144	100.00145	0.00003352
3/13/01	100.00144	100.00139	100.00139	100.00144	100.00142	100.00149	100.00146	100.00147	100.00157	100.00152	100.00146	0.00005662
3/14/01	100.00135	100.00133	100.00135	100.00138	100.00132	100.00133	100.00130	100.00132	100.00128	100.00136	100.00133	0.00002938
3/18/01	100.00156	100.00156	100.00157	100.00161	100.00156	100.00159	100.00159	100.00162	100.00160	100.00164	100.00159	0.00002792
3/26/01	100.00150	100.00147	100.00146	100.00149	100.00147	100.00146	100.00145	100.00146	100.00144	100.00144	100.00146	0.00001962
3/27/01	100.00163	100.00166	100.00169	100.00170	100.00170	100.00166	100.00168	100.00168	100.00171	100.00166	100.00168	0.00002453
Grand Average = 100.001522												

Using analysis of variance (ANOVA) techniques available in Excel[R] spreadsheets [iii], the data were separated into the two components, which are "within" days and "between" days. The "within" day component was calculated directly by the spreadsheet as a variance, which is shown in Figure 2 in bold type as 2.3636E-09 in the MS (mean square) column. The estimation of the "between" days component is slightly more difficult and must be calculated manually from the mean square value, MS(between), shown in the "between" days row. This value is known from statistical theory to estimate the "within" days variance (Var W) plus *r* times the "between day" variance (Var B), where *r* is the number of "within" replicates. See Figure 2 for additional details in calculation of this estimate. Since *r* was 10, the "between" day variance estimate was calculated as 7.4448354E-09. Summing the "within" and "between" variances, the total random variance is 9.8084192E-09. This is equivalent to a standard deviation of 0.00009904 gram or approximately 0.1 milligram. This estimate is considerably larger than the manufacturer's repeatability estimate, which is 3 scale divisions or 0.03 milligram.

Figure 2 – Phase 1 Between/Within Analysis

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Days	1.61305E-06	21	7.6811938E-08	32.5	8.33E-53	1.61
Within Days	4.6799E-07	198	**2.3635838E-09**			
Total	2.08104E-06	219				

MS(Between) = 7.68119E-08 = VarW + 10VarB

Therefore, VarB = { MS-VarW } / 10 = { 7.68119E-08 - 2.3635838E-09 } / 10 = 7.4448354E-09

Total Var = VarW + VarB = 9.8084192E-09. Therefore VarB is 75.9% of Total Var.

From the total random variance and the "between" day component, the "between" day variance was calculated as 75.9% of the total. It should also be noted that an estimate of total variation would be a serious underestimate if one only considered "within" day variation. The "between" day component is 3 times as large and is primarily responsible for the large variation experienced with the balance. As a result, future experimental effort with the new balance was directed towards minimizing the “between” day variance.

Phase II - Experiment and Data Analysis

After receiving the new AX205 balance in early April 2001, it was decided to perform the experiment on the new balance exactly as had been done previously so that proper statistical estimates could be made. Data were collected from April 9 through mid-May and are shown in Table 2 below.

Table 2 – Phase II Replicate Weight Data

Date	1	2	3	4	5	6	7	8	9	10	Average	Std. Dev.
4/9/01	100.00141	100.00141	100.00139	100.00140	100.00141	100.00139	100.00143	100.00142	100.00138	100.00140	100.00140	0.00001505
4/10/01	100.00136	100.00135	100.00134	100.00137	100.00138	100.00139	100.00135	100.00138	100.00142	100.00141	100.00138	0.00002634
4/10/01	100.00147	100.00147	100.00147	100.00148	100.00146	100.00145	100.00146	100.00145	100.00145	100.00147	100.00146	0.00001049
4/10/01	100.00144	100.00142	100.00143	100.00143	100.00142	100.00142	100.00141	100.00138	100.00139	100.00136	100.00141	0.00002540
4/11/01	100.00153	100.00152	100.00153	100.00152	100.00152	100.00152	100.00153	100.00155	100.00152	100.00154	100.00153	0.00001025
4/11/01	100.00151	100.00149	100.00149	100.00149	100.00147	100.00148	100.00150	100.00147	100.00148	100.00147	100.00149	0.00001340
4/12/01	100.00153	100.00151	100.00149	100.00147	100.00148	100.00147	100.00147	100.00147	100.00147	100.00148	100.00148	0.00002050
4/12/01	100.00145	100.00142	100.00145	100.00144	100.00148	100.00141	100.0014	100.00138	100.00146	100.00145	100.00143	0.00003062
4/16/01	100.00144	100.00143	100.00143	100.00142	100.00140	100.00138	100.00141	100.00137	100.00136	100.00137	100.00140	0.00002927
4/17/01	100.00140	100.00139	100.00138	100.00139	100.00138	100.00140	100.00140	100.00142	100.00139	100.00140	100.00140	0.00001179
4/23/21	100.00148	100.00148	100.00147	100.00149	100.00148	100.00151	100.00149	100.00149	100.00147	100.00149	100.00149	0.00001179
4/25/01	100.00142	100.00143	100.00145	100.00146	100.00145	100.00146	100.00146	100.00147	100.00146	100.00147	100.00145	0.00001633
4/26/01	100.00152	100.00152	100.00149	100.00144	100.00145	100.00142	100.00145	100.00143	100.00141	100.00145	100.00146	0.00003913
4/30/01	100.00144	100.00145	100.00144	100.00148	100.00150	100.00141	100.00145	100.00144	100.00143	100.00146	100.00145	0.00002546
5/01/01	100.00145	100.00132	100.00145	100.00142	100.00140	100.00137	100.00140	100.00142	100.00142	100.00136	100.00140	0.00004093
5/02/01	100.00128	100.00132	100.00129	100.00129	100.00132	100.00128	100.00131	100.00131	100.00132	100.00128	100.00130	0.00001767
5/03/01	100.00147	100.00152	100.00150	100.00146	100.00143	100.00146	100.00147	100.00147	100.00145	100.00149	100.00147	0.00002568
5/07/01	100.00140	100.00141	100.00138	100.00140	100.00140	100.00139	100.00140	100.00144	100.00138	100.00138	100.00140	0.00001812
5/08/01	100.00140	100.00142	100.00138	100.00139	100.00138	100.00139	100.00137	100.00138	100.00137	100.00137	100.00139	0.00001588
5/14/01	100.00150	100.00151	100.00144	100.00143	100.00147	100.00144	100.00137	100.00143	100.00145	100.00142	100.00145	0.00004029
5/15/01	100.00144	100.00145	100.00145	100.00144	100.00145	100.00144	100.00145	100.00143	100.00144	100.00145	100.00144	0.00000696
5/16/01	100.00154	100.00148	100.00150	100.00154	100.00153	100.00155	100.00154	100.00155	100.00153	100.00153	100.00153	0.00002246
Grand Average = 100.001436												

From the beginning, the new balance appeared to be much more stable and have less inherent variability. Our feelings about the balance were soon confirmed as we begin calculating the “within” day variations that are shown in Table 2. Data collection continued until May 16 when we had 22 sets of data. As was done previously, a complete statistical treatment was performed on the data, and the analysis is shown in Figure 3.

Figure 3 – Phase II Between/Within Analysis

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Days	1.61305E-06	21	2.83832E-08	50.5	8.03E-68	1.61
Within Days	4.6799E-07	198	5.62086E-10			
Total	2.08104E-06	219				

MS(Between Days) = 2.83832E-08 = VarW + 10VarB

Therefore, VarB = { MS-VarW } /10 = { 2.83832E-08 - 5.62086E-10 } / 10 = 2.78211E-09

Total Var = VarW + VarB = 3.3441939E-09. Therefore VarB is 83.2% of Total Var.

The analysis indicated the new balance was superior to the old in both the “within” and “between” day variation. The “within” day variation improved from a variance of 2.3636E-09 to 5.6209E-10 while the “between” day variation improved from a variance 7.4448354E-09 to 2.78211E-09. Summing as before, we had a total random variance of 3.34419E-09. This is equivalent to a standard deviation of 0.000058 gram or approximately 0.06 milligram, which compares to 0.1 milligram with the first balance.

Phase III - Experiment and Data Analysis

Even though the total variation was improved over the first balance, a calculation of “between” day contribution to the total variation indicated it was still the largest contributor at 83%. As a result, additional effort was undertaken to further improve the day to day balance variation. The balance was placed on a marble slab, a new power supply was obtained from the manufacturer and a field service technician came to the laboratory to perform his own diagnostics. While in the laboratory, the technician re-calibrated the internal weights with OIML Class E2 mass standards. After these modifications, additional experimental data were taken for 22 days, beginning in early August and ending in mid-September. The data are shown in Table 3.

Table 3 – Phase III Replicate Weight Data

Date	1	2	3	4	5	6	7	8	9	10	Average	Std. Dev.
8/07/01	100.00151	100.00149	100.00152	100.00154	100.00153	100.00151	100.00149	100.00151	100.00148	100.00149	100.00151	0.0000195
8/07/01	100.00150	100.00148	100.00148	100.00150	100.00150	100.00148	100.00149	100.00148	100.00147	100.00143	100.00148	0.0000208
8/08/01	100.00150	100.00145	100.00145	100.00142	100.00141	100.00142	100.00144	100.00144	100.00144	100.00145	100.00144	0.0000249
8/08/01	100.00144	100.00143	100.00143	100.00140	100.00141	100.00142	100.00141	100.00141	100.00142	100.00144	100.00142	0.0000138
8/09/01	100.00136	100.00138	100.00138	100.00138	100.00138	100.00138	100.00138	100.00138	100.00138	100.00138	100.00138	0.0000058
8/09/01	100.00142	100.00140	100.00139	100.00141	100.00140	100.00139	100.00140	100.00141	100.00140	100.00140	100.00140	0.0000093
8/13/01	100.00148	100.00147	100.00148	100.00149	100.00149	100.00146	100.00146	100.00145	100.00141	100.00139	100.00146	0.0000336
8/14/01	100.00150	100.00148	100.00146	100.00147	100.00147	100.00146	100.00145	100.00143	100.00144	100.00141	100.00146	0.0000259
8/15/01	100.00141	100.00142	100.00142	100.00141	100.00143	100.00138	100.00135	100.00133	100.00134	100.00134	100.00138	0.0000394
8/20/01	100.00152	100.00150	100.00152	100.00152	100.00152	100.00148	100.00146	100.00144	100.00140	100.00141	100.00148	0.0000471
8/27/01	100.00159	100.00157	100.00157	100.00154	100.00154	100.00155	100.00154	100.00154	100.00155	100.00153	100.00155	0.0000189
8/28/01	100.00148	100.00148	100.00148	100.00149	100.00146	100.00140	100.00148	100.00146	100.00144	100.00143	100.00146	0.0000287
8/29/01	100.00164	100.00164	100.00162	100.00162	100.00163	100.00162	100.00161	100.00161	100.00160	100.00160	100.00162	0.0000144
8/30/01	100.00157	100.00156	100.00157	100.00159	100.00157	100.00160	100.00158	100.00160	100.00157	100.00156	100.00158	0.0000149
9/04/01	100.00159	100.00161	100.00153	100.00152	100.00152	100.00151	100.00151	100.00149	100.00150	100.00152	100.00153	0.0000389
9/05/01	100.00149	100.00151	100.00152	100.00149	100.00150	100.00153	100.00149	100.00149	100.00151	100.00150	100.00150	0.0000144
9/06/01	100.00147	100.00147	100.00146	100.00147	100.00147	100.00148	100.00147	100.00147	100.00145	100.00146	100.00147	0.0000082
9/12/01	100.00154	100.00150	100.00155	100.00154	100.00151	100.00155	100.00153	100.00152	100.00152	100.00151	100.00153	0.0000176
9/13/01	100.00159	100.00156	100.00153	100.00155	100.00154	100.00157	100.00157	100.00156	100.00152	100.00155	100.00155	0.0000206
9/17/01	100.00150	100.00149	100.00143	100.00146	100.00147	100.00142	100.00142	100.00142	100.00142	100.00142	100.00145	0.0000320
9/18/01	100.00150	100.00150	100.00147	100.00148	100.00149	100.00150	100.00147	100.00146	100.00146	100.00146	100.00148	0.0000173
9/19/01	100.00155	100.00152	100.00159	100.00155	100.00155	100.00152	100.00146	100.00147	100.00152	100.00148	100.00152	0.0000412
Grand Average = 100.001484												

The same statistical analysis was performed on the data as was done previously. The analysis is shown in Figure 4. The “between”, “within” and total estimates of random variance were slightly larger than previous, but the differences were determined not to be statistically significant. From the total calculated variance of 4.4178355E-.09, the total random standard deviation was calculated as 0.000066 gram or approximately 0.07 milligram. Apparently, the modifications that were made to the balance and environment had little effect on the random variation of the balance. Having made no improvement in the random variation, we conclude that a standard deviation of 0.06-0.07 milligram is the best we can accomplish with the balance given our current uncontrolled environmental conditions. This uncertainty is approximately twice the “repeatability” value stated by the manufacturer. Additional effects of the environment is given below:

Figure 4 – Phase III Between/Within Analysis

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Days	8.0373E-07	21	3.83E-08	58.3	5.13E-73	1.61
Within Days	1.2992E-07	198	6.56159E-10			
Total	9.3365E-07	219				

MS(Between Days) = 3.82729E-08 = VarW + 10VarB

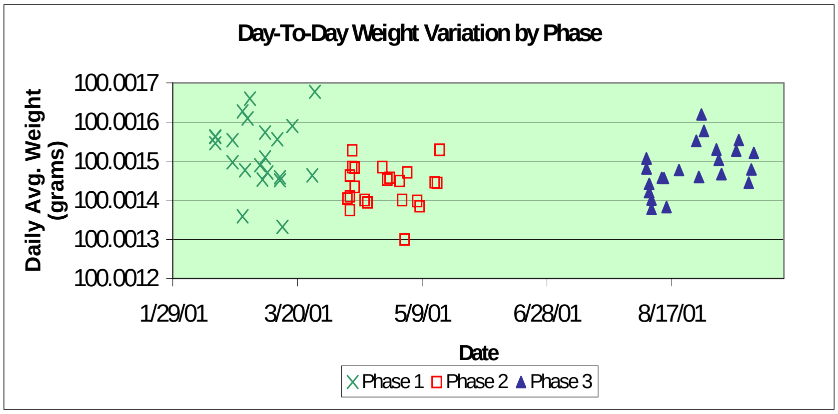
Therefore, VarB = { MS-Var(within) } /10 = { 3.82729E-08 - 6.56159ZE-10 } / 10 = 3.76168E-09

Total Var = VarW + VarB = 4.4178355E-09. Therefore VarB is 85.1% of Total Var.

Environmental Effects on Variation

Day to day variation was experienced in all phases of the experiment. A good summary of the weight variation over time is a plot of daily averages as shown in Figure 5 below.

Figure 5 – Day-to-Day Weight Variation for All Phases



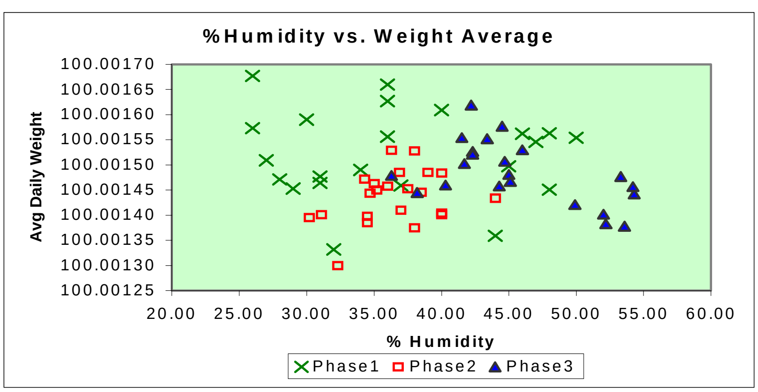
The effect of environmental changes is most likely the cause of the day to day weight variation seen in the data. Table 4 is a summary of the environmental parameters that were measured during Phase I, II and III. They were temperature centigrade (Temp C.), barometric pressure in millimeters (BP) and percent relative humidity (%Humidity). The average gram quantity and standard deviation is shown.

Table 4 – Environmental Data Summary

Environmental Factors				
		Phase I	Phase II	Phase III
Weight (gms.)	Avg.	100.00152	100.00144	100.00148
	Std. Dev.	0.000099	0.000058	0.000066
Temp C	Avg.	23.09	22.67	22.40
	Std. Dev.	0.95	0.89	0.75
BP(mm)	Avg.	1005.1	1007.25	1004.72
	Std. Dev.	4.25	4.65	2.51
% Humidity	Avg.	36.7	36.5	45.8
	Std. Dev.	8.0	3.2	5.4

As one can see, there was some variation in all the environmental factors measured. The AX205 model balance has a temperature compensation feature that should have corrected for any temperature variation of 1-degree C. The barometric pressure differences will cause air buoyancy effects, but their significance should be at a lesser order of magnitude than we are concerned with. However, humidity could possibly affect the weights by moisture regain on the surface of the internal calibration weights or the surface of the nominal 100-gram test weight. Figure 6 shows that the highest humidity standard deviation was during Phase I, least in Phase II and slightly more

Figure 6 – Day-to-Day Weight Variation for All Phases



in Phase III. Using an F-test on the corresponding variances, the humidity standard deviations were found to be statistically significant from one another with 95% confidence. The day-to-day weight variations follow the same pattern in magnitude (See Figure 5 or Table 4), and suggest that the humidity variation was a large contributor to the day-to-day variability.

Bias Considerations

Our discussion so far has centered only on the random uncertainty of the balance. Now we will briefly turn our attention toward systematic uncertainty or bias. Of most interest is a comparison of the second balance before (Phase II) and after calibration (Phase III). The grand averages for these phases from Tables 2 and 3 are 100.001436 and 100.001484 respectively, from which we calculate a difference of 0.0000473 gram or 0.05 milligram. Using a t-test, this difference is significant which indicates a shift in the average weight, possibly due to the re-calibration by the technician. However, the Phase III average was nearer to the certified weight value of 100.00151 grams than before the calibration.

Conclusions

We have discussed in detail an experiment to empirically determine the total uncertainty in a new balance. Throughout the experiment, we have discovered many things.

The first discovery was the excessive variation in the new balance. This led to a replacement by the manufacturer. If we had begun using the balance without any experimental work, we would have introduced unwanted variation into the pipette calibrations that we had planned. We are sure the balance manufacturer does his best to produce a quality product and probably does most of the time. Maybe we were unlucky, but without the experiment, the balance could have led to inferior pipette calibrations.

With the replacement balance we discovered that the “between” day portion of the uncertainty was significant and was about 3 times that of the repeatability. Since this variation is real, it has an impact on our measurements. If we had used just the repeatability portion, we would have grossly underestimated the actual uncertainty of the balance and its impact of the quality of gravimetric pipette calibrations done with it.

After the environmental modifications and calibration, we discovered that we were unable to improve the balance uncertainty. We are still sure that variation is related in some ways to other environmental conditions such as temperature, pressure, and humidity. Our data also indicate some correlations with these variables. However, we did not have further means of control. Our estimates of variation had value then for the current environmental condition even though they are larger than the repeatability suggested by the manufacturer. We conclude then that a good estimate of the uncertainty of a balance can only be determined empirically in the environment in which it will be ultimately used. Also, our experience indicated that a balance’s uncertainty is always more than the manufacturer’s repeatability specification.

References

[i] J. P. Clark and A.H. Shull, “Analytical Chemistry Measurement Assurance Programs: More Than Just Measurement Control Programs”, Proceedings of the Measurement Science Conference, Pasadena, CA, 1997.

[ii] Box, G. E. P., Hunter, W. G., and Hunter, J. S., *Statistics for Experimenters*, John Wiley & Sons, Inc., 1978.

[iii] Walpole, R. E., and Myers, Raymond H., *Probability and Statistics for Engineers and Scientists*, Macmillan Publishing Co., Inc., 1972.